Joint Reaction by Formaldehyde

AUTHOR(S):

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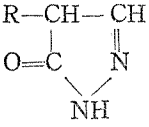
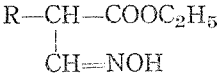
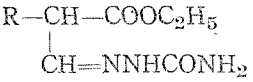
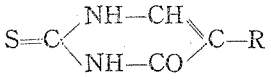
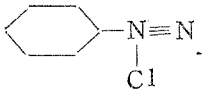
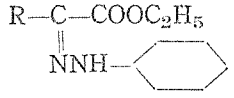
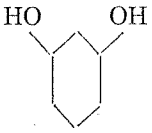
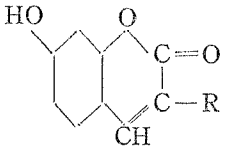
The mixture of 50 g. of ethyl stearate and 12 g. of ethyl formate was added in dry ether under ice-cooling in which 3.8 g. of metallic sodium was suspended and was stood for several days. The obtained Na-salt was dissolved in water, neutralized with HCl and extracted with ether. Twenty seven grams of ethyl α-formyl stearate was obtained. Yield 49.6%, m.p. 64°C.

II. Reactions of Ethyl α-Formylstearate.

Ethyl α-fformylstearate was reacted with various passive components, the results are summerized in the following:

	Passive component	Product	Yield(%) m.p.(C)	N% found (calcd.)
1.	NH_2NH_2		46.8 108	8.65 (9.02)
2.	NH_2OH		67.0 55	3.65 (3.94)
3.	$NH_2NHCONH_2$		35.9 73	10.10 (10.57)
4.	NH_2CSNH_2		42.5 97	7.37 (7.96)
5.			30.7 56	6.33 (6.70)
6.			61.8 75	401 found) mol. 386 calcd.) wt.

17. Joint Reaction by Formaldehyde

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Formaldehyde is a distinguished active component and joints any two passive components (P_1H and P_2H) in the manner as follows:

$$P_1 + CH_2O \longrightarrow P_1 - CH_2OH \xrightarrow{P_2H} P_1 - CH_2 - P_2 + H_2O$$

By this joint reaction a great many jointed compounds should be produced, combining any pair of passive components. But till now, relatively few cases have been investigated and there remains yet a wide unresearched field. The anthors have undertaken some research in this field and want to report here a part of the experimental results.

As P_1H acetone was chosen mainly, *i. e.* reactions between γ-ketobutanol (1) and anothor passive component were investigated.

1. Reaction between (I) and acetoacetic ester.

$$CH_3COCH_2{-}CH_2OH + CH_2\begin{matrix}COCH_3\\COOC_2H_5\end{matrix}$$

$$\longrightarrow CH_3COCH_2CH_2{-}CH\begin{matrix}COCH_3\\COOC_2H_5\end{matrix}$$

$$\longrightarrow CH_3COCH_2CH_2CH_2COCH_3$$

The mixture of γ-ketobutanol and acetoacetic ester was refluxed for 3 hrs., the intermediate β-acetylethylacetoacetate was identified by the quantitative carbonyl-group analysis and ketonic decomposition, producing diacetylpropane (m. p. of di-semi carbazone: 210~3°).

2. Reaction between (I) and malonic acid.

$$CH_3COCH_2CH_2OH + CH_2(COOH)_2$$

$$\longrightarrow CH_3COCH_2CH_2CH(COOH)_2$$

$$\longrightarrow CH_3COCH_2CH_2CH_2COOH$$

The reaction mixture was refluxed for many hours in a steam bath and as product the γ-acetyl butyric acid was detected.

3. Reaction between (I) and NaCN.

$$CH_3COCH_2CH_2OH + NaCN \longrightarrow CH_3COCH_2CH_2CN$$

$$\longrightarrow CH_3COCH_2CH_2COOH$$

The γ-ketobutanol was added gradually to the hot solution of NaCN, evolution of ammonia was recognized and as the product laevulinic acid was detected.

4. Reaction between (I) and thioglycolic acid.

$$CH_3COCH_2CH_2OH + HSCH_2COOH$$

$$\longrightarrow CH_3COCH_2CH_2{-}S{-}CH_2COOH$$

The reaction mixture was refluxed and as the product acetylethyl-thioglycolic acid was detected (neutralization value; found, 335, calculated, 346).

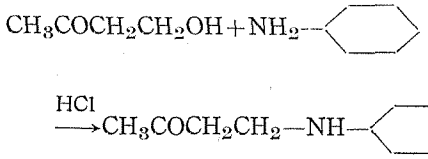
5. Reaction between (I) and nitromethane.

$$CH_3COCH_2CH_2OH + CH_3NO_2$$

$$\xrightarrow{K_2CO_3} CH_3COCH_2CH_2CH_2NO_2$$

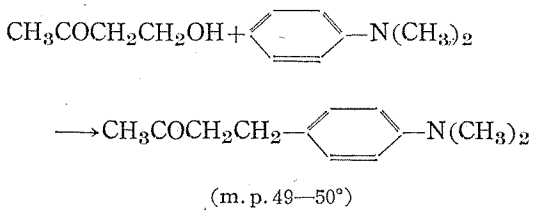
As the product nitropentanone-2 was detected (m. p. of semicarbazone: 138-40°)

6. Reaction between (I) and aniline.

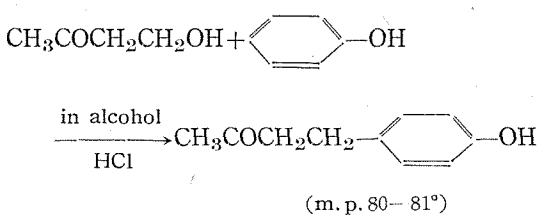


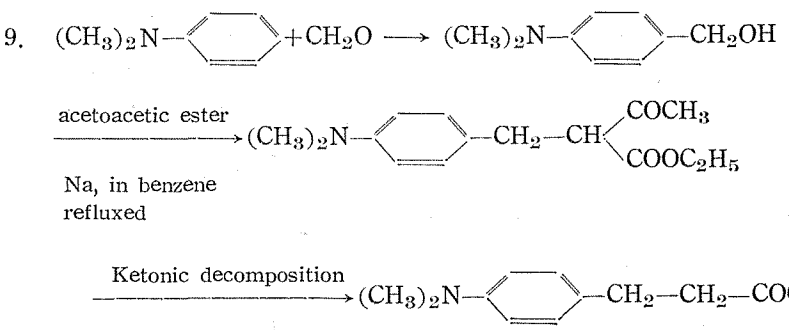
As the product acetylethylaniline was detected (m.p. of semicarbazone: 160°) Similar results were obtained with *o*-toluidine.

7. Reaction between (I) and N-dimethylaniline.



8. Reaction between (I) and phenol.



9. 

10.